U.G. 2nd Semester Examinations 2022

CHEMISTRY (Honours)

Paper Code : CEMH DC-T3

[CBCS]

Full Marks : 25   Time : Two Hours

The figures in the margin indicate full marks.
Candidates are required to give their answers
in their own words as far as practicable.

1. Answer any *five* questions from the following :   1×5=5

   (a) If the electron of a hydrogen atom is present in the first orbit, the total energy of the electron in CGS system is —

      (i) $- e^2/r$

      (ii) $- e^2/r^2$

      (iii) $- e^2/2r$

      (iv) $- e^2/4r^2$

   (b) The ground state term symbol of Nitrogen is —

      (i) $^3P_0$

      (ii) $^4P_{3/2}$

      (iii) $^1P_1$

      (iv) $^4S_{3/2}$

   (c) If covalent radius of Au(Z=79) is 134 pm, Allred-Rochow electronegativity of Au is —

      (i) 1.41

      (ii) 1.31

      (iii) 0.87

      (iv) 3.21

(d) Which one of the following species will show strongest acidity?

    (i) $[Na(H_2O)_n]^+$

    (ii) $[Al(H_2O)_6]^{3+}$

    (iii) $[Ni(H_2O)_6]^{2+}$

    (iv) $[Mn(H_2O)_6]^{2+}$

(e) The correct order of the decreasing ionic radii among the following isoelectronic species are —

    (i) $Ca^{2+} > K^+ > S^{2-} > Cl^-$

    (ii) $Cl^- > S^{2-} > Ca^{2+} > K^+$

    (iii) $S^{2-} > Cl^- > K^+ > Ca^{2+}$

    (iv) $K^+ > Ca^{2+} > Cl^- > S^{2-}$

(f) The pH of a 1×10^{-8} M HCl solution is close to —

    (i) 8.0

    (ii) 7.1

    (iii) 6.9

    (iv) 6.0

(g) With respect to periodic properties, the correct statement is —

    (i) Electron affinity is in the order : $F > O > Cl$

    (ii) First ionization energy is in the order : $Al > Mg > K$

    (iii) Atomic radius is in the order : $N > P > As$

    (iv) Ionic radius is in the order : $K^+ > Ca^{2+} > Mg^{2+}$

(h) From the given reduction potential values, ferricyanide can oxidise iodide to iodine in presence of Zn^{2+} ion is due to formation of which of the following :

$$E^0_{\left(\left[Fe(CN)_6^{3-}\right]/\left[Fe(CN)_6^{4-}\right]\right)} = 0.36V \text{ and } E^0_{\left(I_2/2I^-\right)} = 0.54V$$

    (i) $K_2Zn_3[Fe(CN)_6]_2$

    (ii) $K_2Zn[Fe(CN)_6]$

    (iii) $K_2Zn_2[Fe(CN)_6]_2$

    (iv) $KZn[Fe(CN)_6]$

2. Answer any *four* questions from the following :   2×4=8

(a) Given that $E°$ for : MnO_4^- (aq) + $8H^+$ (aq) + $5e^-$ $\rightleftharpoons$ Mn^{2+} (aq) + $4H_2O$ (l) is 1.51 V, calculate the reduction potential, $E°$, in a solution of pH 2.5 and in which the ratio $[Mn^{2+}] : [MnO_4^-]$ = 1 : 100.

(b) Explain why electron affinity of Mn^{3+} is greater than that of Fe^{3+}?

(c) Boric acid is weak acid in aqueous solution. Why does its acidity increase significantly in presence of ethylene glycol?

(d) Consider the following pair : $(H_3Si)_2O$, $(H_3C)_2O$. Explain why silyl ether is the weaker Lewis base?

(e) Ba^{2+}, Ca^{2+}, Sr^{2+} all can be precipitated as their carbonates in $NH_4Cl – NH_4OH$ medium with $(NH_4)_2CO_3$ reagent in analytical group but not Mg^{2+}. Justify the statement.

(f) HNO_3, HCl and H_2SO_4 appear equally strong in water, but their strengths differ in acetic acid medium. Justify.

(g) Metallic tin reacts with cold dilute nitric acid to form stannous nitrate and ammonium nitrate. Write the chemical equation for the above reaction and balance it by ion electron method.

(h) Using the concepts of shielding and penetration, explain why a ground state configuration of $1s^2 2s^1$ for a Li atom is energetically preferred over $1s^2 2p^1$.

3. Answer any *two* questions from the following :   2×6=12

(a) (i) The Balmer series of spectral lines for hydrogen appear in the visible region. What is the lower energy level that these electronic transitions start from, and what transitions correspond to the spectral lines at 379.0 nm and 430.0 nm respectively?

    (ii) What is Hammett acidity function? Show how it compares the strengths of strong acids. (iii) There is a decrease in first ionization energy from Be to B, and Mg to Al. Give reasons.   2+2+2

(b) (i) Prove that disproportionation reaction in aqueous solution is thermodynamically favourable for the system given below :

    Cu^+ (aq) $\rightleftharpoons$ Cu (s) + Cu^{2+} (aq)

    $[E°_{Cu^{2+}(aq)/Cu^+(aq)}$ = 0.153V and $E°_{Cu^+(aq)/Cu(s)}$ = 0.512V]

    Would you expect similar disproportionation in ammonia solution?

    (ii) Account for the larger increase in effective nuclear charge for a 2p electron on going from B to C compared with a 2s electron on going from Li to Be. Justify.

    (iii) Estimate pK_a values of H_3PO_4 using Pauling's formula.   3+2+1

(c) (i) Discuss the physical significance of and ψ and ψ^2.

(ii) Calculate Allred-Rochow electronegativity of Zn taking its covalent radius as 125 pm.

(iii) A the polarity of B-X bonds is in the order B-F > B-Cl > B-Br, but Lewis acidity shows the sequence $BF_3 < BCl_3 < BBr_3$. Explain. 2+2+2

(d) (i) Calculate the change in pH at the end point, when 100 mL 0.1 (N) NaOH is titrated with 0.1 (N) CH_3COOH ignoring the change in volume. [pK_a (CH_3COOH) = 4.73]. What indicator will you use and why?

(ii) Why atomic radii of Zr and Hf are almost identical?

(iii) What is the significance of m_l? 3+2+1

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